Supporting Information

Galvanic cell reaction driven electrochemically doping of TiO_2 nanotube photoanodes for enhanced charge separation

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Experiment Methods

Preparation of TiO_2 nanotube array electrodes. The electrochemical anodic oxidation method was used to fabricate the TiO_2 nanotube arrays film.[1] To remove the surface oxidation layer, the titanium sheet (0.2 mm thickness, 99.5% purity) was first chemically polished in the solution containing HF, HNO_3, and deionized water (1:2:7 in volume) for 30 s. The resulting titanium sheets were ultrasonically cleaned with acetone, ethanol, and deionized water, and then were anodized in 250 mL NH_4F-containing ethylene glycol (EG) solution (1g NH_4F, 245 mL EG, 5mL deionized water) at 60 V for 15 min at room temperature and the counter electrode was a platinum plate. The as-anodized samples were thoroughly cleaned with deionized water and then annealed in air at 450 ^oC for 2 h with a heating rate of 10 $^oC\ min^{-1}$.

$NaBH_4$ treatment. The conductor parts of the as obtained sample where no nanotubes grown were polished with sandpaper to remove the TiO_2 compact layer on the surface of Ti sheet formed during heat treatment. The one that whole sample including nanotubes and conductor parts was immersed in 0.5 M $NaBH_4$ solution (W-TiO_2). The other one the conductor parts on the back and front of the photoanode were thoroughly sealed by insulating tape and only nanotubes on the sample can contact $NaBH_4$ electrolyte (O-TiO_2). For comparison, commercial anatase TiO_2 nano powders (0.1 g) were added to 50 mL 0.5 M $NaBH_4$ solution under magnetic stirring for a relative long time 3 h at room temperature.

Electrochemical doping. The TiO_2 nanotubes electrode as the working electrode were immersed in 1 M NaOH solution. Then a negative bias -1.35 V was applied in the dark at room temperature for 10 ~ 60 s.[2]

TiO_2 nanotube array characterizations. The morphologies of the TiO_2 nanotube photoanodes were observed by field-emission scanning electron microscope (FE-SEM; Nova NanoSEM 230, FEI). Crystal phases of these samples were determined using an X-ray

diffractometer (XRD, Rigaku Ultima Ⅲ, Japan) operated at 40 kV and 40 mA using Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with monochromatized Al Kα excitation. The spectral positions were corrected by normalizing the C1s spectrum at 284.6 eV, and a Shirley background was used for peak fitting. The UV-Vis absorption spectra were obtained by ultraviolet-visible spectrophotometer (UV, Shimadzu UV-2550). Electron paramagnetic resonance (EPR) was conducted with an X-band EPR spectrometer (EMX-10/12, Bruker, German) operating at a microwave frequency of 9.49 GHz at 110 k.

Electrochemical and photoelectrochemical characterization. A CHI760E electrochemical workstation (Shanghai Chenhua Company, Shanghai, China) was used to conduct the electrochemical and photoelectrochemical measurements, which were performed in a standard three-electrode cell at room temperature. The electrode except the semiconductor-electrolyte interface was thoroughly sealed with silica gel or black insulating tape. A platinum plate and saturated Ag/AgCl were used as counter and reference electrodes, respectively. All the potentials are described by referring to the Ag/AgCl reference electrode. A 500 W Xe lamp was used as the light source for photocurrent measurements. The irradiated area was circular with area of 0.28 cm^2 and photocurrent densities were normalized to 1 cm^2. Oxidation–reduction potential was measured by open circuit potential (OCP) mode. Mott-Schottky curves were measured using an electrochemical analyzer (2273, Princeton Applied Research, AMETEK, USA). The electrochemical impedance spectra (EIS) were measured using an electrochemical analyzer (Solartron 1260 + 1287, AMETEK, USA) with a 10 mV amplitude perturbation and frequencies between 100 kHz and 0.1 Hz

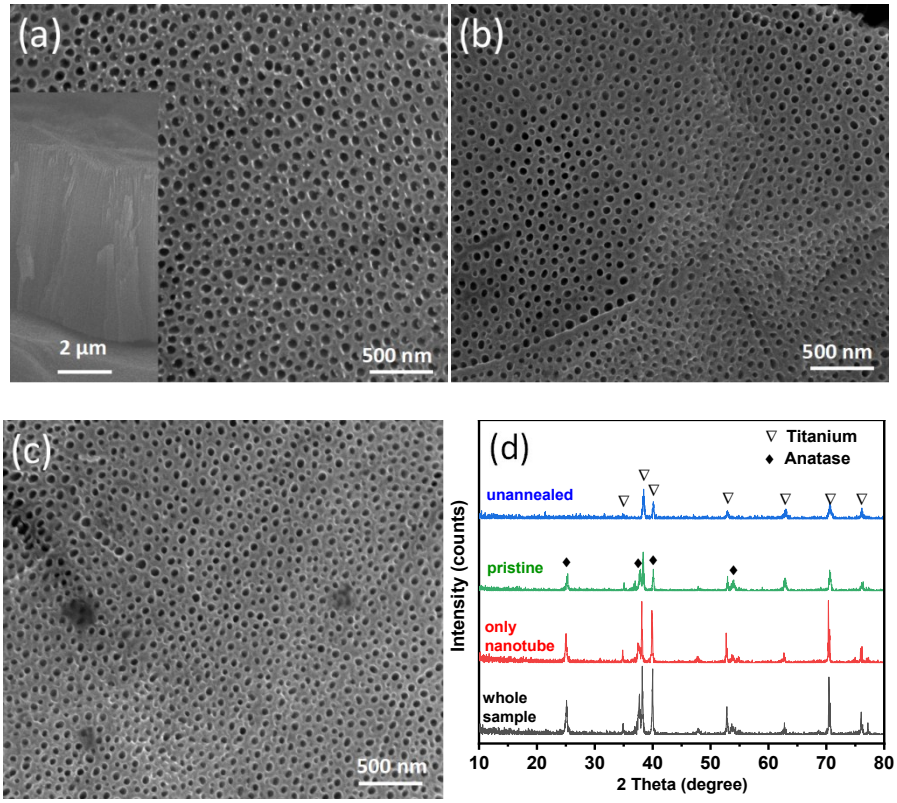

Fig. S1 SEM images of TiO_2 nanotube array electrode. (a) The as-obtained sample. The inset shows a cross-section SEM image. (b) W-TiO_2 electrode after immersing in $NaBH_4$ for 1 h. (c) O-TiO_2 electrode after immersing in $NaBH_4$ for 1 h. (d) XRD patterns. The sample after anodic oxidation (blue line) and after annealing (green line) in air at 450 °C for 2 h, the TiO_2 nanotube electrode after $NaBH_4$ treatment for 1 h, O-TiO_2 (red line) and W-TiO_2 (black line).

The samples obtained by anodic oxidation without annealing in air is essentially amorphous because all the diffraction peaks are assigned to Ti substrate. After heating in air at 450 °C for 2 h, the amorphous film became crystallized single-phase TiO_2 with anatase structure (JCPDS Card No. 21-1272). Morphology and structural properties of the samples were almost no varied after $NaBH_4$ treatment.

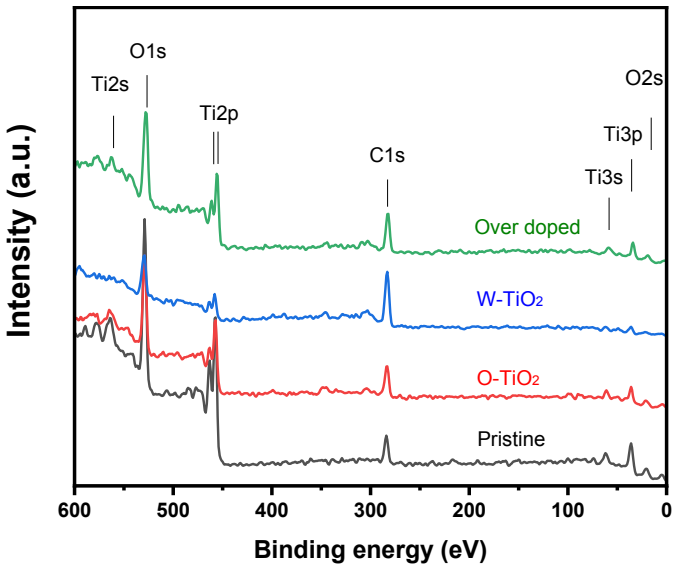

Fig. S2 Wide XPS spectrum. The pristine TiO_2 nanotube photoanodes, O-TiO_2, W-TiO_2 and electrode electrochemical over doped in aqueous 1 M NaOH at -1.75 V 90 s.

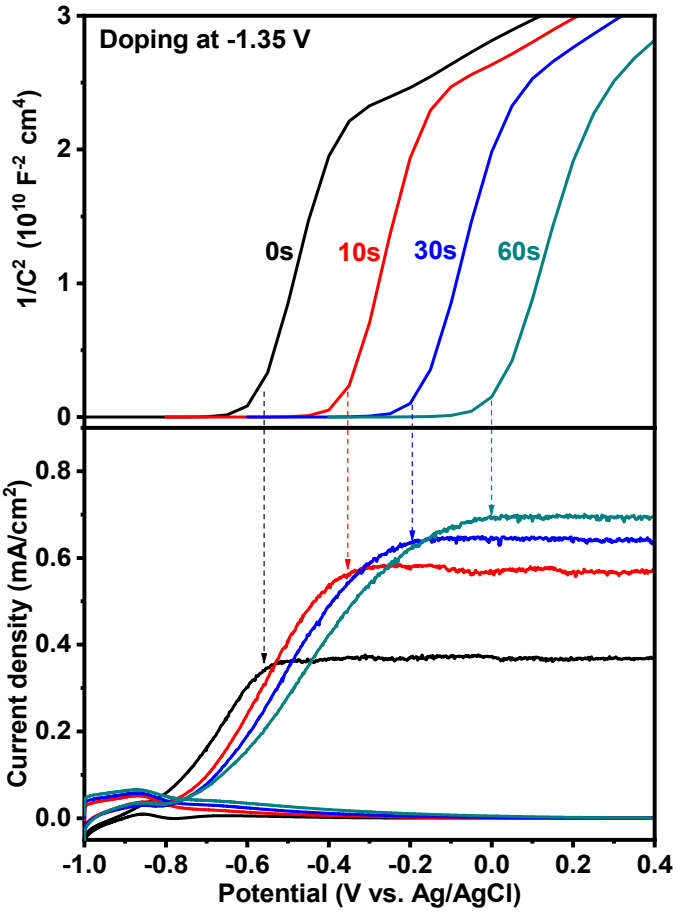

Fig. S3 The correlation of Mott-Schottky plots (top) and photocurrent density curves (bottom) of TiO_2 nanotubes electrode after electrochemical doping in 1 M NaOH solution at -1.35 V for 0, 10, 30, and 60 s. Scan rate: 20 mV s^{-1}.[2]

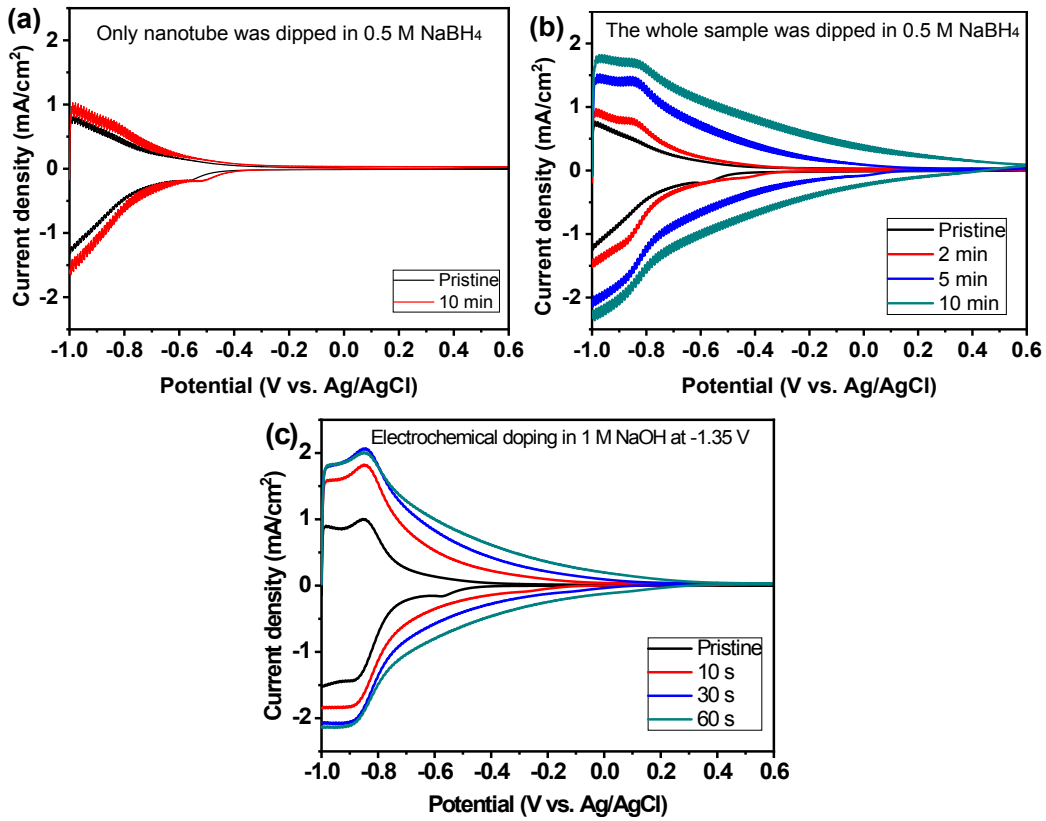

Fig. S4 (a) Cyclic voltammetry (CV) curves of the O-TiO_2 samples before and after $NaBH_4$ treatment for 10 min. (b) CV curves of the W-TiO_2 samples before and after $NaBH_4$ treatment for 2, 5, and 10 min. (c) CV curves of the samples before and after electrochemical doping in aqueous 1 M NaOH at -1.35 V for 10, 30, and 60 s. Scan rate: 500 mV s^{-1}. We can find that after $NaBH_4$ treatment the CV curves for W-TiO_2 are very similar with the TiO_2 nanotube array after electrochemical doping.

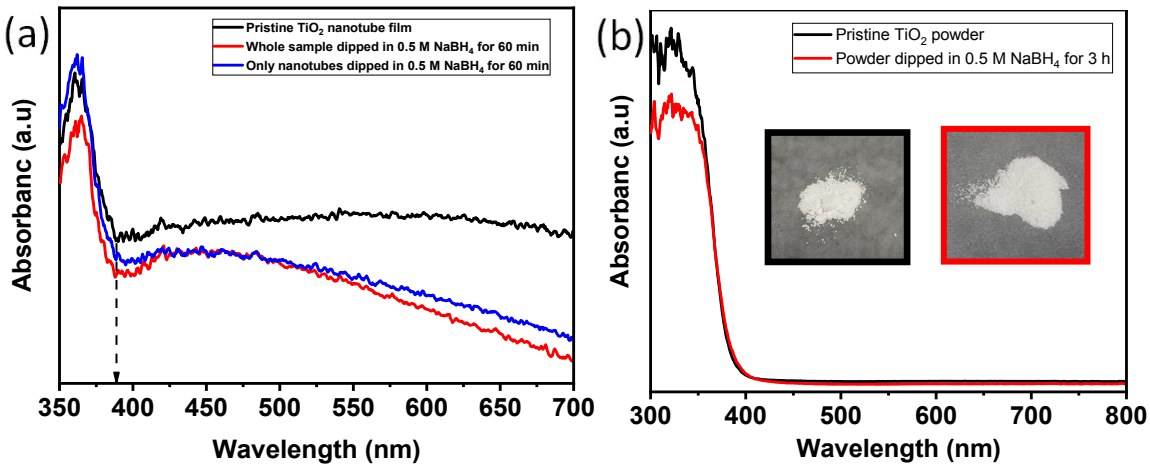

Fig. S5 (a) The UV-visible diffuse reflection spectra of TiO_2 nanotube array before and after $NaBH_4$ treatment for 60 min of W-TiO_2 and O-TiO_2 electrodes. (b) The UV-visible diffuse reflection spectra of TiO_2 nanoparticles before and after $NaBH_4$ treatment for 3 h. Inset pictures were the photo of the samples.

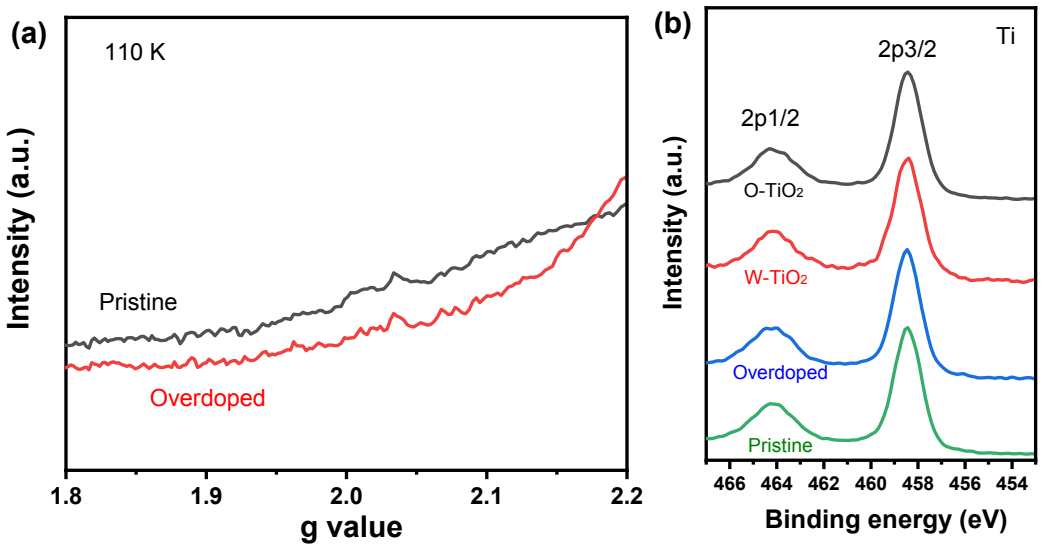

Fig. S6 (a) EPR spectra for pristine and electrochemical overdoped TiO_2 nanotube photoanodes. (b) XPS spectra of Ti2p.

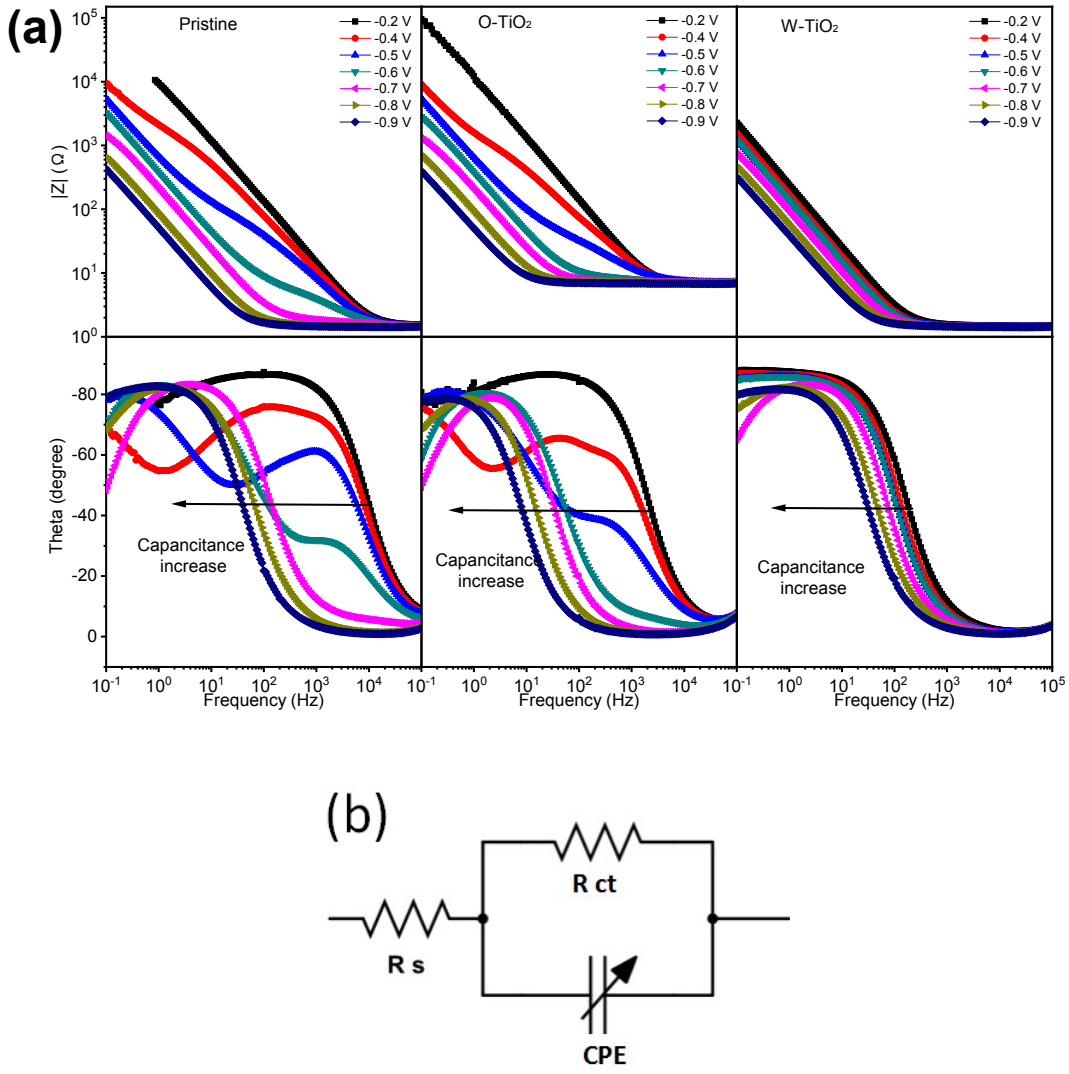

Fig. S7. Electrochemical impedance diagrams (Bode representation) of the as obtained (right), O-TiO_2 (mid) and W-TiO_2 (left) nanotube electrodes measured in 1 M NaOH in the dark. The active area of the samples was 0.28 cm^{-2} (b) Equivalent circuits used to simulate the EIS data. R_s: resistance from electrolyte and semiconductor- substrate electrical connection; R_{ct}: interfacial charge transfer resistance between semiconductor and electrolyte; CPE: capacitance for space charge layer or surface states of TiO_2 nanotube electrode.

For the pristine and O-TiO_2 when at the potential positive to -0.5 V vs. Ag/AgCl the capacitance decreases dramatically. Because at this potential charges in the surface states and nanotube walls were fully depleted which could not respond to the electrical signal. In addition, for W-TiO_2 nanotube electrodes charges in surface states and nanotube walls were not depleted

at the potential window we used because the high surface states density formed by electrochemical doping induced by the galvanic cell reaction during $NaBH_4$ treatment. The result is consistent with the M-S and CV results. So, we believe abundant surface states formed on W-TiO_2 *via* an electrochemical doping reaction induce by a galvanic cell reaction during $NaBH_4$ treatment.

Fitting parameters of EIS data obtained by using the equivalent circuit proposed in **Fig. S7**

Samples	Potential (V vs. Ag/AgCl)	CPE		$R_{ct,bulk}$ (KΩ)	R_s (Ω)
		Q ($\mu\Omega^{-1}s^n$)	n		
Pristine TiO_2 nanotubes	-0.9	3469	0.95	3.5	1.4
	-0.8	2083	0.94	2.3	1.5
	-0.7	825.9	0.95	2.3	1.7
	-0.3	38.0	0.88	46.8	1.4
	-0.2	16.0	0.96	48.4	1.5
O-TiO_2	-0.9	3714	0.93	3.6	6.8
	-0.8	1916	0.94	2.3	7.1
	-0.7	494.9	0.92	7.6	7.7
	-0.3	27.3	0.89	29.6	6.6
	-0.2	13.6	0.97	74.2	7.0
W-TiO_2	-0.9	4684	0.94	3.5	1.4
	-0.8	3062	0.94	2.6	1.4
	-0.7	1842	0.96	1.9	1,4
	-0.6	1484	0.96	7.7	1.5
	-0.5	1131	0.99	10.8	1.5
	-0.4	934.3	0.99	21.1	1.5
	-0.3	770.1	0.99	31.9	1.5
	-0.2	657.9	0.99	57.4	1.5

*The active area of the samples was 0.28 cm^{-2}

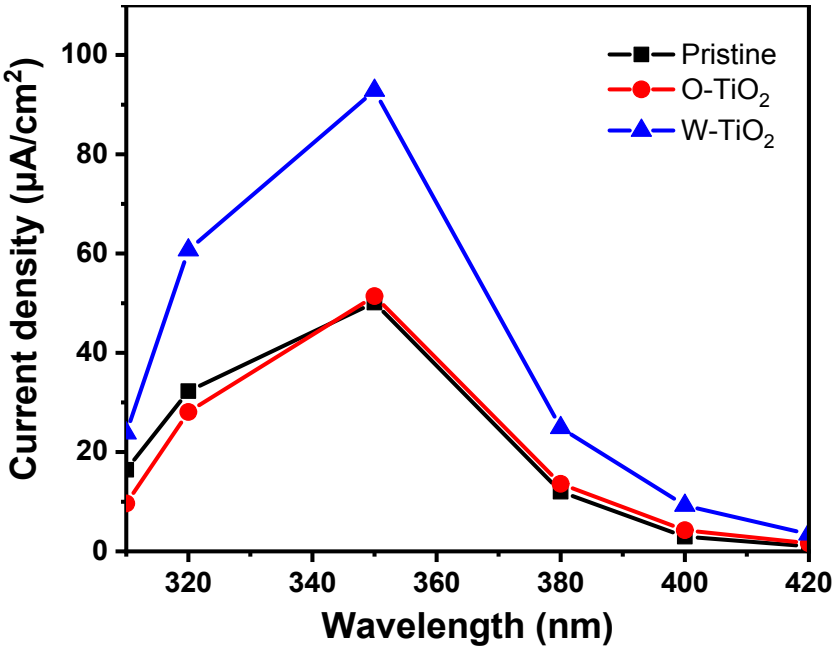

Fig. S8 Under different monochromatic light irradiation, the photocurrents for pristine TiO_2 nanotube photoanodes, O-TiO_2 and W-TiO_2 photoanodes after 10 min $NaBH_4$ treatment. The increased current density was not come from the visible light contribution. After $NaBH_4$ treatment, the charge separation efficiency for W-TiO_2 photoanodes at the ultraviolet region increased dramatically comparing to O-TiO_2 photoanodes.

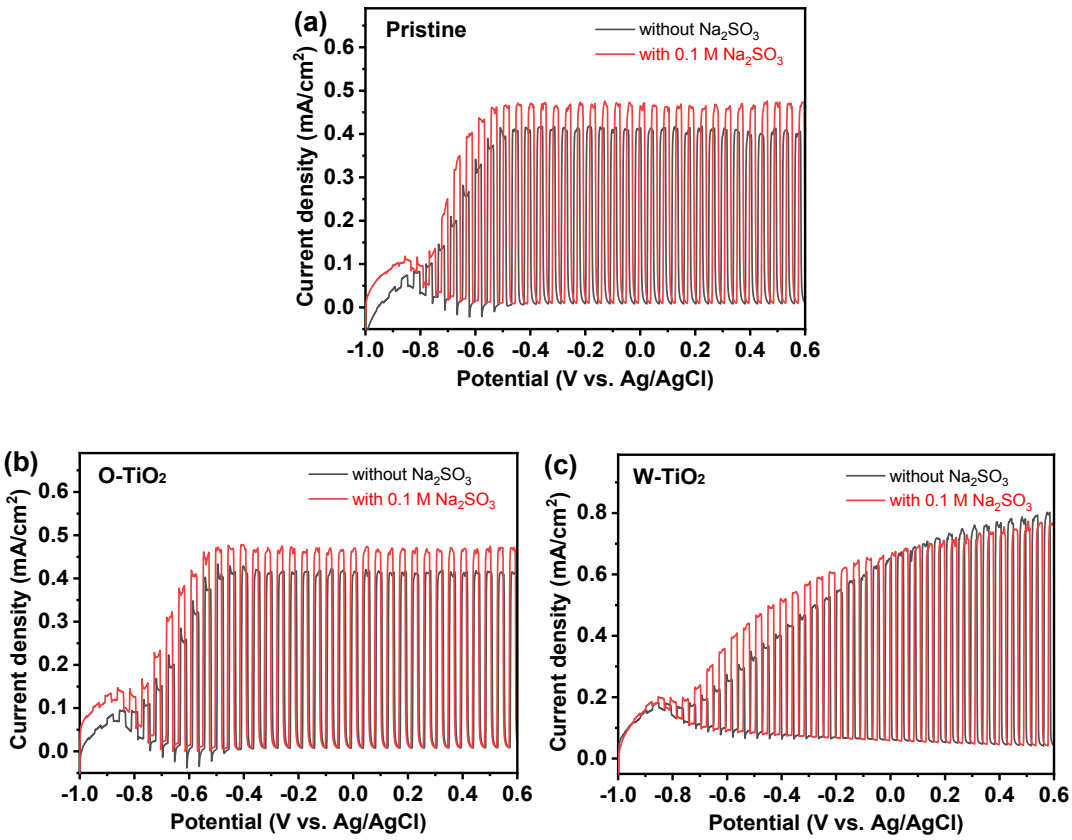

Fig. S9. Effect of sulfite ions on photocurrent density for TiO_2 nanotube electrodes (a) pristine TiO_2 nanotube photoanodes, (b) O-TiO_2 and (c) W-TiO_2 photoanodes after 10 min $NaBH_4$ treatment. A slight photocurrent difference was observed at the electrolyte with or without Na_2SO_3 hole scavenger, indicating that $NaBH_4$ treatment does not change the OER kinetics. The increasing of charge separation efficiency was the reason of the enhanced photocurrent density for W-TiO_2 photoanodes.

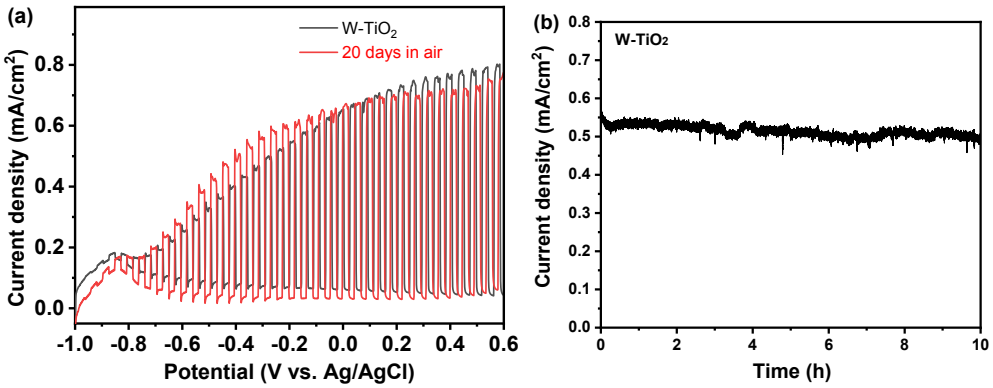

Fig. S10 (a) Photocurrent density measured in 1 M NaOH for W-TiO_2 nanotube electrodes just after 10 min $NaBH_4$ treatment and the same photoanodes put in air for 20 days. (b) Chronoamperometry measurement for W-TiO_2 photoanode held at 0.2 V versus Ag/AgCl in NaOH for 10 h.

References

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2 H. Zhu, M. Zhao, J. Zhou, W. Li, H. Wang, Z. Xu and L. Lu, *Appl. Catal. B Environ.*, 2018, **234**, 100–108.